

# Kinetic Theory of Reactive Molecular Gases

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## 1.0 INTRODUCTION

In high enthalpy gaseous flows associating high velocities and/or high temperatures, physical and chemical processes such as vibrational excitation, dissociation, ionisation and various reactions, can take place. The characteristic times of these processes have often the same order of magnitude as the “mechanical” or aerodynamic characteristic times, so that these flows constitute typical non-equilibrium media.

The best way for analysing these reactive flows in continuous or “collisional” regime consists in using a statistical approach by considering the macroscopic quantities as local averages of various properties of elementary particles (molecules, atoms, ions,...) and by taking into account their interactions resulting from their “collisions”. Thus, the Boltzmann equation seems to be an appropriate tool for the description of these flows.

Among the methods used for solving the Boltzmann equation, the Chapman-Enskog method, consisting in expanding the distribution function in a series of a “small parameter”  $\varepsilon_I$  equal to the ratio of the characteristic time between collisions to a reference flow time has known a great success. However, in the past, it has been generally limited to the case where only one single type of collision is present in the medium. Thus, at relatively low temperature, when the elastic collisions are “dominant”, the behaviour of the system is correctly described by Navier-Stokes equations in which transport terms are satisfyingly calculated by the Chapman-Enskog method [1], [2], [3].

Now, when physical and chemical processes take place, the ratio of their characteristic times  $\varepsilon_{II}$  (inelastic and/or reactive collisions) to the reference flow time can take any value. The problem first is to compare  $\varepsilon_I$  and  $\varepsilon_{II}$  and to insert the terms of physical and chemical production in the hierarchy imposed by the expansion in a series of  $\varepsilon_I$  and then to compute the modifications brought to the Navier-Stokes system and to the transport terms [4], [5].

It is obvious that a great variety of non-equilibrium situations may exist due to the numerous possible multi-scale physical and chemical processes. However, it is imperative that the number of collision types should be restricted to only two (collisions I and II), in order to avoid an expansion beyond the first two terms in the Chapman-Enskog expansion (Navier-Stokes level) [6].

The strict application of the Chapman-Enskog method to non-equilibrium situations is first presented: it leads to two main general approaches called WNE and SNE methods depending on the degree of non-equilibrium considered : WNE for “weak” non-equilibrium situations and SNE for “strong” ones [7]. In the application of these methods to concrete cases, it is obvious that they do not match in the intermediate situations. That is why, a generalized Chapman-Enskog method (GCE), capable of realizing this matching is finally presented and developed [8], [9].

On the other hand, as it is impossible, in the framework of this lecture to analyse all possible situations, two typical situations are examined hereafter: first the case of vibrational non-equilibrium in pure gases

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and gas mixtures and second the case of dissociating pure gases. A few results are also given for more complex systems [10], [11].

At last, applications of the results obtained from the GCE method are presented for hypersonic flows in which vibrational and chemical non-equilibriums simultaneously take place: they concern the kinetic rate constants, the transport coefficients and more generally the characteristics of hypersonic flows such as shock waves, boundary layers and flows around bodies [12], [13], [14].

## 2.0 GENERALITIES ON NON-EQUILIBRIUM FLOW REGIMES

### 2.1 The Boltzmann Equation in Reactive Systems

In a flow of gas mixture, the Boltzmann equation governing the distribution function  $f_{ip}$  of the particles of the component  $p$  in the quantum state  $i$  can be simply written

$$\frac{df_{ip}}{dt} = J \quad , \quad (1)$$

where the quantum level  $i$  includes a rotational level  $i_r$ , a vibrational level  $i_v$  and, eventually an electronic level  $i_e$ :

$$i = (i_r, i_v, i_e)$$

The collisional term  $J$  includes all types of collision, elastic, inelastic and reactive, that is

$$J = J_T + J_R + J_V + J_C + \dots \quad , \quad (2)$$

where  $J_T$  represents the collisional balance of particles undergoing a velocity change only (elastic collisions),  $J_R$  and  $J_V$  the balance of collisions with rotational and vibrational change respectively (inelastic collisions),  $J_C$  the balance of collisions with species change (reactive collisions), etc...

These collisions may be subdivided in more specific types, such as VV collisions (both interacting molecules change their vibrational level), TV (only one molecule change its level) or resonant collisions (they interchange their level), etc....

These collisions of course have different probabilities to occur, so that they have different characteristic times (probable times between specific collisions),  $\tau_T$ ,  $\tau_R$ ,  $\tau_V$ ,  $\tau_{VV}$ ,  $\tau_C$ ,... which may differ by an order of magnitude. Thus, two examples are given in Figs.1 and 2 for  $O_2$  and  $N_2$  respectively.

In these conditions, we may write the Boltzmann equation (1) in the following dimensionless form:

$$\frac{df_{ip}^*}{dt^*} = \frac{1}{\varepsilon_T} J_T^* + \frac{1}{\varepsilon_R} J_R^* + \frac{1}{\varepsilon_V} J_V^* + \frac{1}{\varepsilon_C} J_C^* + \dots \quad , \quad (3)$$

or any other form adapted to the specific case considered.

In Eq.(3), we have:  $\varepsilon_T = \tau_T / \theta$ ,  $\varepsilon_R = \tau_R / \theta$ ,  $\varepsilon_V = \tau_V / \theta$ , .....

where  $\theta$  represents the “aerodynamic” reference time, depending on the problem under study and that may take considerably different values.

As stated in the introduction, we will consider only two collisional characteristic time scales  $\varepsilon_I$  and  $\varepsilon_{II}$ , so that all collisions are classified in two groups, for example elastic collisions in group I and inelastic in group II; or TRV collisions in group I and reactive in group II, etc... Thus, we will simply write Eq.3 in the following form:

$$\frac{df_{ip}^*}{dt^*} = \frac{1}{\varepsilon_I} J_I^* + \frac{1}{\varepsilon_{II}} J_{II}^* \quad (4)$$

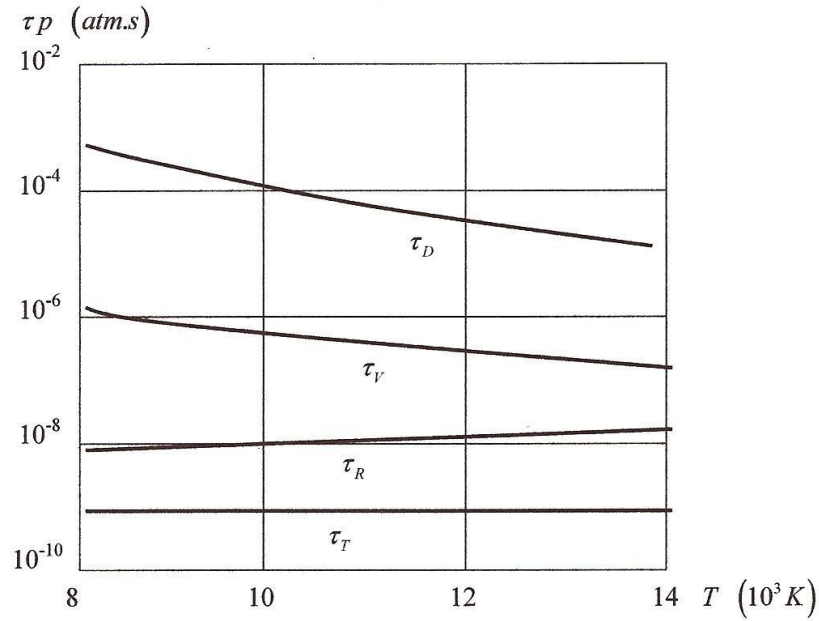


Figure 1: Translation, rotation, vibration, dissociation characteristic times (Nitrogen)

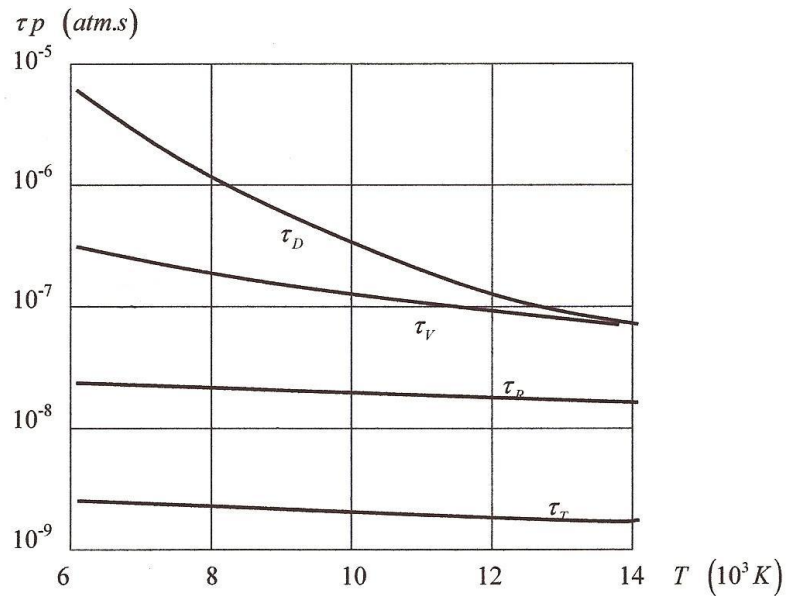


Figure 2: Translation, rotation, vibration, dissociation characteristic times (Oxygen)

## 2.2 Chapman-Enskog expansion: Flow regimes

Considering flows in “collisional regime”, we may assume that the collisions I are dominant (the most probable), so that  $\varepsilon_I \ll 1$ , ( $\tau_I \ll \theta$ ). In this case, we can classically expand  $f_{ip}$  in a series of

$$\varepsilon_I = \varepsilon, \text{ that is } f_{ip}^* = f_{ip}^{0*} + \varepsilon f_{ip}^{1*} + \dots,$$

or, stopping the expansion at the first order:

$$f_{ip}^* = f_{ip}^{0*} (1 + \varepsilon \varphi_{ip}^*) \quad (5)$$

where  $f_{ip}^{0*}$  is the zero order distribution function and  $f_{ip}^{1*}$  the first order one, with  $f_{ip}^{1*} = f_{ip}^{0*} \varphi_{ip}^*$  and  $\varphi_{ip}^* \ll 1$ .

Now, we have to substitute the expansion (5) in Eq.(4) and to introduce the collisional term II into the expansion. In order to do that, there are three possibilities: 1)  $\varepsilon_{II} \ll 1$ , that is  $\varepsilon_{II} \ll \frac{1}{\varepsilon}$ , 2)  $\varepsilon_{II} \ll 1$ , that is  $\varepsilon_{II} \ll \varepsilon$ , or 3)  $\varepsilon_{II} \ll 1$ .

In the first case, we obtain the following system giving successively  $f_{ip}^{0*}$  and  $\varphi_{ip}^*$ :

$$\begin{aligned} J_I^0 &= 0 \\ \frac{df_{ip}^{0*}}{dt} &= J_I^1 \end{aligned} \quad (6)$$

Thus, the collisions II have no influence on the zero and first order distribution function. This corresponds to the “frozen case” for the collisions II.

On the contrary, in the case 2), the collisions II play the same role as the collisions I in the determination of the distribution function, since we have the following system to solve:

$$\begin{aligned} (J_I + J_{II})^0 &= 0 \\ \frac{df_{ip}^{0*}}{dt} &= (J_I + J_{II})^1 \end{aligned} \quad (7)$$

In the intermediate case 3), we have the following system:

$$\begin{aligned} J_I^0 &= 0 \\ \frac{df_{ip}^{0*}}{dt} &= J_I^1 + J_{II}^0 \end{aligned} \quad (8)$$

Thus, we can dismiss the frozen case which brings nothing new in comparison with the classical CE method used when only one type of collision is considered.

Considering now the case 2), we easily find that, at the zero order of the system (7), the Euler equations govern the system with an equilibrium distribution (levels and species) for the zero order distribution function  $f_{ip}^{0*}$ . On the contrary, in the case 3), at zero order of the system (8), the Euler equations must be closed by kinetic equations (species) and/or relaxation equations giving the evolution of “populations” due to collisions II in the time scale  $\theta$ : this corresponds to a non-equilibrium situation.

At first order, the linear integral-differential equations allow to obtain the perturbation  $\varphi_{ip}$  and the Navier-Stokes equations govern the system, but kinetic and/or relaxation equations are still necessary in the case 3) and, moreover, the collisions I and II appear in a different way in cases 2) and 3).

It is also to be noted that, whatever the form of  $f_{ip}^0$  is, in equilibrium or not, the first order solution always exhibits a non-equilibrium which remains small because of the linearisation. Therefore, the solution obtained from Eqs.(7) corresponds to a weak non-equilibrium case called WNE regime and the solution corresponding to Eqs.(8) is denoted SNE regime (strong non-equilibrium).

The cases presented above may hide complex situations: first, the indices I and II represent various types of collisions, either simple (T, R, V, C), complex (TR, TRV,...), or particularized (VV, resonant...); thus the specific situations are numerous.

Furthermore, each type of regime may apply to one or several types of collisions. For example, we call (WNE)<sub>I</sub>+(SNE)<sub>II</sub> a weak non-equilibrium regime for the collisions I and a strong non-equilibrium for the collisions II. If, as a standard example, we consider the case of a pure gas in a strong vibrational non-equilibrium, we call this case (WNE)<sub>TR</sub>+(SNE)<sub>v</sub>. In the same way, if the chemical non-equilibrium is significant at the zero order and if the vibrational non-equilibrium is “less” important, we call this regime (WNE)<sub>TRV</sub>+(SNE)<sub>C</sub>, or simply (WNE)<sub>v</sub>+(SNE)<sub>C</sub>, etc... Simple typical examples are presented below.

### 3.0 VIBRATIONALLY RELAXING GASES

#### 3.1 Zero Order Solutions

Pure diatomic gas flows are first considered. The equilibrium zero order solution (Maxwell-Boltzmann) is well known and is obtained from the equation:  $J_{TRV}^0 = 0$ . Thus, the “normal” solution is

$$f_i^0 = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -\frac{mu^2}{2kT} \right) \frac{g_{i_r} \exp(-\varepsilon_{i_r}/kT)}{Q_R} \frac{\exp(-\varepsilon_{i_v}/kT)}{Q_V} \quad (9)$$

with usual notations:  $n$  number density,  $m$  molecular mass,  $T$  temperature,  $\varepsilon_{i_r}$ ,  $\varepsilon_{i_v}$  rotational and vibrational energies per molecule,  $Q_R(T)$ ,  $Q_V(T)$  rotational and vibrational partition functions,  $g$  statistical weight. One single temperature  $T$  is defined. The macroscopic quantities are given by Euler equations.

##### 3.1.1 General non-equilibrium situations

The most general non-equilibrium situation corresponds to the equation  $J_{TR}^0 = 0$ , that is the collisions I include the T (elastic) and R collisions and the collisions II include all V collisions. Thus, we have

$$f_i^0 = n_{i_v} \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -\frac{mu^2}{2kT} \right) \frac{g_{i_r} \exp(-\varepsilon_{i_r}/kT)}{Q_R} \quad (10)$$

The corresponding macroscopic equations are the Euler equations and the relaxation equations giving the vibrational populations  $n_{i_v}$ , that is

$$\frac{\partial n_{i_v}}{\partial t} + \frac{\partial n_{i_v} \mathbf{V}}{\partial \mathbf{r}} = \sum_{i_r, j, k, l} n_k n_l a_{k,l}^{i,j} - n_i n_j a_{i,j}^{k,l}, \quad (11)$$

where  $V$  is the macroscopic velocity,  $a_{ij}^{kl}$  and  $a_{kl}^{ij}$  the collision rate coefficients corresponding to the transitions  $i, j \leftrightarrow k, l$ , independent of the populations.

### 3.1.2 Particular non-equilibrium situations

Now, if particular highly probable collisions with vibrational exchanges are included in collisions I, the vibrational populations take specific forms. Thus, three important examples are briefly presented hereafter.

- TV collisions are dominant and are included in collisions I; we have:

$$J_{TV} = 0$$

In this case, the solution is given by the relation (9), which means that the TV collisions are sufficient to establish an equilibrium regime.

- VV collisions are dominant [15] and are included in collisions I; in this case, we find a non-equilibrium distribution (10), with

$$n_{i_v} = n \frac{\exp(-\varepsilon_{i_v}/kT + Ki_v)}{\sum_{i_v} \exp(-\varepsilon_{i_v}/kT + Ki_v)} \quad (\text{Treanor distribution}) \quad (12)$$

The macroscopic parameter  $K$  is given by the following unique relaxation equation:

$$\frac{dI_v}{dt} = [\exp(-K) - 1] \sum_{i_v} a_{i_v+1}^{i_v} n_{i_v+1},$$

where  $I_v$  is a mean quantum number defined as  $nI_v = \sum_{i_v} n_{i_v} i_v$  and where, here, only monoquantum transitions are assumed to take place.

This distribution presents a minimum for a particular quantum number, so that “population inversions” are possible, especially in gas mixtures.

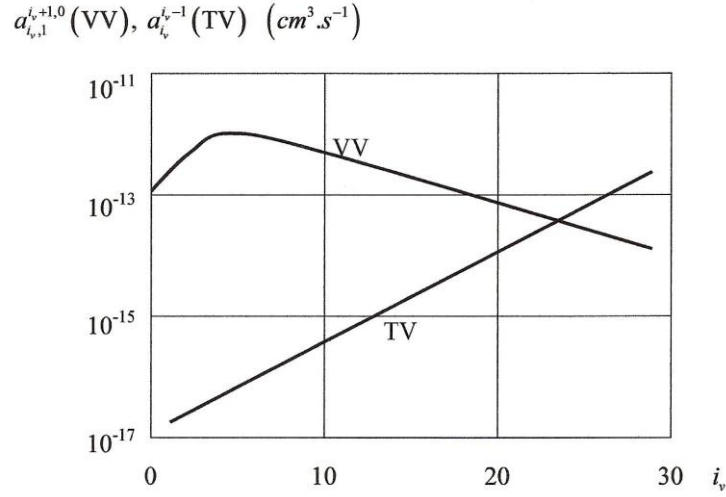
- Resonant collisions ( $i_v + j_v \leftrightarrow j_v + i_v$ ) are dominant and are included in collisions I. In this case, we find a Boltzmann distribution at a “vibrational temperature”  $T_v$ , that is

$$n_{i_v} = n \frac{\exp(-\varepsilon_{i_v}/kT_v)}{\sum_{i_v} \exp(-\varepsilon_{i_v}/kT_v)} \quad (13)$$

This temperature is also given by a unique relaxation equation giving the mean vibrational energy  $E_v$ .

In order to complete the previous equations, a physical oscillator model is required. For example, the choice of the simple harmonic oscillator model, leading to the Landau-Teller relaxation equation simplifies the problems but may mask detailed (and essential) features of the relaxation...

On the other hand, before choosing a global model (Boltzmann, Treanor,...), it is essential to determine its domain of validity: thus, for example at low temperature, the VV collisions are more probable for the low levels and the TV collisions more probable for the highest levels at high temperature: An example [16] is presented in Fig.3.



**Figure 3: TV and VV collision rates ( $N_2 - N_2$ ,  $T=1000K$ )**

From a general point of view, the macroscopic parameters appearing in  $f_i^0$  are given by the conservation equations including Euler and relaxation equations corresponding to the Fredholm alternative of the first order equation of the system (8), that is

$$\int_v \left( \frac{df_i^0}{dt} - J_i^0 \right) C_i dv = 0, \quad (13)$$

where  $C_i$  are the collisional invariants of collisions I.

### 3.2 First order solutions. Transport Terms

#### 3.2.1 WNE Case

This is a relatively classical case. We start from the equilibrium zero order solution (9) and we have to solve the equation  $\frac{df_i^0}{dt} = J_{TRV}^1$ . Taking into account the form of the known terms  $\frac{df_i^0}{dt}$  and various constraints related to the definition of macroscopic parameters with  $f_i^0$ , we can write the perturbation  $\varphi_i$  in the following form:

$$\varphi_i = A_i \frac{1}{T} \frac{\partial T}{\partial \mathbf{r}} \cdot \mathbf{u} + B_i \frac{\partial \mathbf{V}}{\partial \mathbf{r}} : \mathbf{u}\mathbf{u} + D_i \frac{\partial \mathbf{V}}{\partial \mathbf{r}}, \quad (14)$$

where  $X_i = A_i, B_i, D_i$  are unknown scalar functions of  $\mathbf{r}, t, \mathbf{u}, \varepsilon_i, \varepsilon_i$ . Classically, each term  $X_i$  is expanded in Sonine-Wang-Chang-Uhlenbeck polynomials [17], that is

$$X_i = \sum_{m,n,p} x_{mnp} S_T^m P_R^n P_V^p, \quad (15)$$

with  $x = a, b, d$ . In the expansion (15), only zero and first order terms are retained, i. e.  $x_{000}, x_{100}, x_{010}, x_{001}$ ; each index corresponds to the order of expansion respectively for translation,



rotation and vibration. These terms are determined from particular equations involving the corresponding terms of  $\frac{df_i^0}{dt}$ . Because of the properties of the orthogonal expansion (15), they can be expressed as functions of “collisional integrals”, defined as follows:

$$\langle \dots \rangle = \left( \frac{kT}{\pi m} \right)^{1/2} \sum_{i,j,k,l} \frac{\bar{n}_i \bar{n}_j}{n^2} \int_{\Omega, \gamma} \exp(-\gamma^2) \gamma^3 (\dots) I_{i,j}^{k,l} d\Omega d\gamma, \quad (16)$$

where the populations  $\bar{n}_i, \bar{n}_j$  are in equilibrium and where  $I_{i,j}^{k,l}$  is the differential cross-section of the transition  $i, j \rightarrow k, l$ ,  $\gamma = \left( \frac{m}{2kT} \right)^{1/2} g$  a dimensionless relative velocity and  $\Omega$  the diffusion solid angle. These integrals involve all types of collision.

At the macroscopic level, the Navier-Stokes equations govern the evolution of macroscopic quantities  $n, V, T$  and the corresponding transport terms are the following:

$$\begin{aligned} \text{Stress tensor: } \mathbf{P} &= p\mathbf{I} + \mathbf{P}', \text{ with } \mathbf{P}' = -2\mu \frac{\partial \mathbf{V}}{\partial \mathbf{r}} - \eta \frac{\partial \mathbf{V}}{\partial \mathbf{r}} \mathbf{I} \\ \text{Heat flux: } \mathbf{q} &= \mathbf{q}_T + \mathbf{q}_R + \mathbf{q}_V = -\lambda \frac{\partial T}{\partial \mathbf{r}}, \end{aligned} \quad (17)$$

where the viscosity and conductivity coefficients  $\mu, \eta, \lambda$  are also known functions of collisional integrals of type (16). More details and approximate expressions may be found in Ref.24. Thus, we can see that  $\mu \propto \tau_T p$  and  $\eta \propto \tau_V p$ . It is important to note that a “weak” rotational and vibrational non-equilibrium appears at first order of the expansion of the distribution function: since generally  $\tau_V \propto \tau_R$ , we find for the vibrational non-equilibrium:

$$E_V - \bar{E}_V \propto \tau_V \frac{\partial V}{\partial \mathbf{r}} \quad (18)$$

Temperatures, specific to each energy mode  $T_T, T_R, T_V$  may thus be defined at first order but this is independent of the definition of a single “average” temperature  $T$ , common to the three modes and given by Navier-Stokes equations. It may be also noted that the difference between  $T_T$  and  $T_R$  is of the order of  $\tau_R$ , so that it is generally possible to define a common temperature  $T_{TR}$ , which is of course not the case for  $T_T$  and  $T_V$ .

### 3.2.2 SNE Case

We start from the zero order non-equilibrium solution (10), with vibrational population given by Eq. (13) in which the dominant collisions include the vibrational resonant transitions: this enables us to preserve the notion of vibrational temperature  $T_V$ . Thus, the first order equation is the following:

$$\frac{df_i^0}{dt} = J_{TR}^1 + J_V^0 \quad (19)$$

Taking into account the zero order terms  $\frac{df_i^0}{dt} - J_V^0$ , we can write the perturbation  $\phi_i$  in the following form:

$$\varphi_i = A_i \frac{1}{T} \frac{\partial T}{\partial \mathbf{r}} \cdot \mathbf{u} + B_i \frac{\partial \mathbf{V}}{\partial \mathbf{r}} : \mathbf{u}\mathbf{u} + D_i \frac{\partial \mathbf{V}}{\partial \mathbf{r}} + F_i \frac{1}{T_V} \frac{\partial T_V}{\partial \mathbf{r}} \cdot \mathbf{u} + G_i \quad , \quad (20)$$

where, as above,  $X_i = A_i, B_i, D_i, F_i, G_i$  are unknown scalar functions of  $\mathbf{r}, t, u, \varepsilon_i, \varepsilon_{i_v}$ .

The last two terms in Eq.(20) arise from the vibrational non-equilibrium already present at zero order.

Expanding  $X_i$  as above (15), we can also express the coefficients  $x$  as functions of collisional integrals: however, as expected from Eq.(19), these coefficients (except  $g$ ) depend on integrals including only the collisions I, that is here the TR collisions, noted  $\langle \dots \rangle_{TR}$ . The coefficients  $g$  directly depend on the vibrational relaxation, because of the  $J_V^0$  term.

The macroscopic conservation equations are also the Navier-Stokes equations, completed by relaxation equation giving  $e_v$  or  $T_v$ , that is

$$n \frac{dE_v}{dt} + \frac{\partial \mathbf{q}_v}{\partial \mathbf{r}} = \sum_i \varepsilon_{i_v} \int (J_V^0 + J_V^1) d\mathbf{v} \quad (21)$$

Of course, a physical oscillator model is necessary.

Moreover, the transport terms in the Navier-Stokes equations become

$$\text{Stress tensor: } \mathbf{P} = p\mathbf{I} - 2\mu \frac{\partial \mathbf{V}}{\partial \mathbf{r}} - \left( \eta \frac{\partial \mathbf{V}}{\partial \mathbf{r}} - p_R \right) \mathbf{I} \quad (22)$$

Heat fluxes :  $\mathbf{q} = \mathbf{q}_T + \mathbf{q}_R + \mathbf{q}_V$  , with

$$\begin{aligned} \mathbf{q}_T &= -\lambda_T \frac{\partial T}{\partial \mathbf{r}} - \lambda_{TV} \frac{\partial T_V}{\partial \mathbf{r}} \\ \mathbf{q}_R &= -\lambda_R \frac{\partial T}{\partial \mathbf{r}} - \lambda_{RV} \frac{\partial T_V}{\partial \mathbf{r}} \\ \mathbf{q}_V &= -\lambda_{VTR} \frac{\partial T}{\partial \mathbf{r}} - \lambda_V \frac{\partial T_V}{\partial \mathbf{r}} \end{aligned} \quad (23)$$

Thus, in the stress tensor (22) we find the “usual” terms and a “relaxation pressure” term  $p_R$  (related to  $J_V^0$ ). In the heat flux expressions (23), we find cross terms depending on both temperature gradients. However, as already discussed, the transport coefficients  $\mu, \eta, \lambda \dots$  include only TR collisions (and resonant V collisions). The bulk viscosity  $\eta$  for example depends only on  $\tau_R$ .

Thus, starting from zero order solutions, either in equilibrium or not, we find structural differences in the description of non-equilibrium situations at first order. This is summarized in Table I.

Method	WNE	SNE
<b>Zero order</b>	$J_{TRV}^0 = 0$ TRV equilibrium, with single temperature $T$ . Euler equations	$J_{TR}^0 = 0$ TR equilibrium, with common temperature $T$ . Vibrational non-equilibrium, with temperature $T_V$ . Euler equations, with vib. relaxation equation
<b>First order</b>	$\frac{df_i^0}{dt} = J_{TRV}^1$ Weak RV non-equilibrium. Navier-Stokes equations	$\frac{df_i^0}{dt} = J_{TR}^1 + J_V^0$ Weak R non-equilibrium. Navier-Stokes equations, with vib.relaxation equation
<b>Transport</b>	Transport terms $\mu, \eta, \lambda$ depending on TRV collisions. Heat fluxes depending on the gradient of $T$	Transport terms $\mu, \eta, \lambda_T, \lambda_R, \lambda_V$ depending on TR collisions Heat fluxes depending on the gradients of $T$ and $T_V$

**Table I**  
**Comparison of WNE and SNE methods for vibrationally relaxing gases**

It is thus obvious that there is no matching between both first order solutions when  $T_V \rightarrow T$ . That is why, a generalized Chapman-Enskog method (GCE) is proposed hereafter.

### 3.2.3 GCE Method

The matching between WNE and SNE cases is simply realized by adding a  $J_{II}^1$  term in the linearized equation of the SNE system (8), so that this system becomes:

$$\begin{aligned}
 J_I^0 &= 0 \\
 \frac{df_i^0}{dt} &= J_I^1 + J_{II}^0 + J_{II}^1
 \end{aligned} \tag{24}$$

At zero order, we have the SNE solution covering, as previously discussed, the non-equilibrium and equilibrium situations (Euler system + kinetic and/or relaxation equations). At first order, far from equilibrium the  $J_{II}^1$  term is negligible and we find the SNE solution, but close to equilibrium  $J_{II}^0 \rightarrow 0$  and the first order solution is the WNE solution.

The first order equation of the system (24) is however more difficult to solve than in the WNE or SNE cases because of the structure of the operator  $J_{II}^1$ . Thus, this operator, contrary to  $J_I^1$  is not a

self-adjoint operator, but it may be decomposed into two operators; among them the dominant term  $J_{II}^{A1}$  is self-adjoint and the other may be neglected. Finally, in the present case of vibrational non-equilibrium, we can write the system in the following way:

$$\begin{aligned} J_{TR}^0 &= 0 \\ \frac{df_i^0}{dt} &= J_{TR}^1 + J_V^0 + J_V^{A1} \end{aligned} \quad (25)$$

As previously discussed, the zero order solution of the system (25) is the SNE solution (13) with Euler and relaxation equations. The perturbation  $\varphi_i$  is given by Eq.(20) and we have the same equations for the coefficients  $X_i$ , but, in these equations, the operator  $J_{TR}^1$  is replaced by  $J_{TR}^1 + J_V^{A1}$ . Thus, solving the equation systems giving the coefficients  $x$ , we have to add collisional integrals  $\langle \dots \rangle_V$  to collisional integrals  $\langle \dots \rangle_{TR}$  similar to integrals (16), that is:

$$\langle \dots \rangle_{TR} = \left( \frac{kT}{\pi m} \right)^{1/2} \sum_{i,j,k,l} \left[ \frac{\bar{n}_i \bar{n}_j}{n^2} \int_{\Omega, \gamma} \exp(-\gamma^2) \gamma^3 (\dots) I_{i,j}^{k,l}(TR) d\Omega d\gamma \right] \quad (26)$$

$$\langle \dots \rangle_V = \left( \frac{kT}{\pi m} \right)^{1/2} \sum_{i,j,k,l} \left\{ \frac{\bar{n}_i \bar{n}_j n_{i_v} n_{j_v}}{n^4} \frac{1}{2} \left[ 1 + \exp \left( \Delta \varepsilon_v \left( 1 - \frac{T}{T_v} \right) \right) \times \int_{\Omega, \gamma} \exp(-\gamma^2) \gamma^3 (\dots) I_{i,j}^{k,l}(V) d\Omega d\gamma \right] \right\}, \quad (27)$$

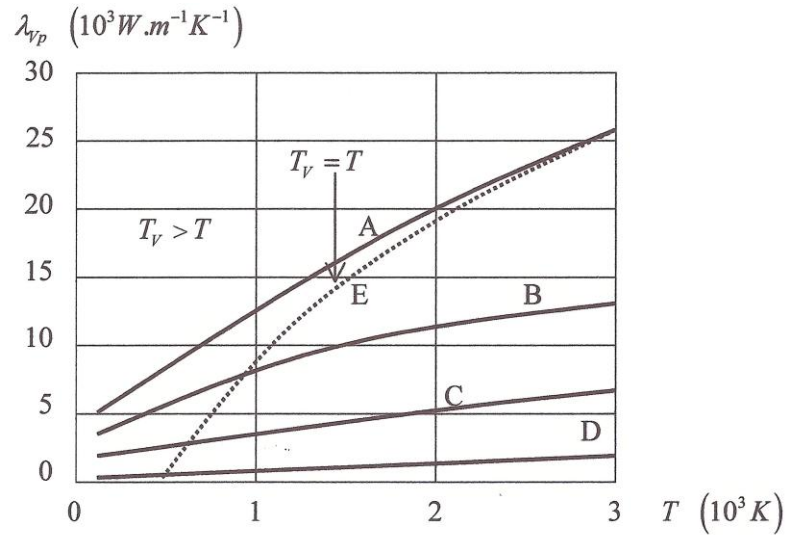
where  $\Delta \varepsilon_v = \frac{\varepsilon_{k_v} + \varepsilon_{l_v} - \varepsilon_{i_v} - \varepsilon_{j_v}}{kT} \neq 0$  and where  $n_{i_v}, n_{j_v}$  are vibrational non-equilibrium populations.

Thus, in integrals  $\langle \dots \rangle_V$  the non-equilibrium appears explicitly. Navier-Stokes equations, of course, remain valid as well as relaxation equations similar to Eq.(21), but the transport coefficients such as  $\mu, \eta, \lambda \dots$  depend on the relaxation explicitly. For example, the viscosity coefficient  $\mu$  may be written as follows:

$$\mu = \mu_{TR} \frac{1}{1+R}, \quad (28)$$

where  $R$  represents the ratio of two integrals similar to (26) and (27), that is  $R = \frac{\langle \phi \rangle_V}{\langle \phi \rangle_{TR}}$ .

For the heat transfer terms, we find expressions similar to those of the SNE system (23), but, when  $T_v \rightarrow T$ , we find the expressions of the WNE case (17) for the conductivity coefficients. Approximate expressions may be obtained and the GCE method can be extended to gas mixtures: details may be found in Ref.10. An example of vibrational conductivity is represented in Fig.4.



**Figure 4: Vibrational conductivity of nitrogen in a mixture (air)**  
 (  $A : T_v = 3000K$ ,  $B : T_v = 1000K$ ,  $C : T_v = 800K$ ,  $D : T_v = 500K$ ,  $E : T_v = T$  )

## 4.0 DISSOCIATING GASES

### 4.1 (WNE)<sub>v</sub>+(SNE)<sub>C</sub> Case

We consider dissociating polyatomic gases; as generally the characteristic chemical times are larger than vibrational relaxation times (Figs.1 and 2), we consider a WNE case for vibration and a SNE case for chemistry, that is a (WNE)<sub>v</sub>+(SNE)<sub>C</sub> case. For a molecular component  $p$ , we have therefore the following system:

$$\begin{aligned} J_{TRVp} &= 0 \\ \frac{df_{ip}^0}{dt} &= J_{TRVp}^1 + J_{Cp}^0 \end{aligned} \quad (29)$$

At zero order, we have a Maxwell-Boltzmann distribution (9) and corresponding Euler equations closed by kinetic equations of the following type:

$$\frac{\partial \rho_p}{\partial t} + \frac{\partial \cdot \rho_p \mathbf{V}}{\partial \mathbf{r}} = \dot{w}_p = \sum_{i_p} m_p \int_{v_p} J_{Cp}^0 d\mathbf{v}_p \quad (30)$$

Considering first only a dissociating pure gas, we have two species, molecules  $p$  and atoms  $q$ . Neglecting the recombination process, we simply have

$$\frac{\dot{w}_p}{m_p} = -k_D n_p^2, \quad (31)$$

where  $k_D = \bar{k}_D(T)$  is the Arrhenius dissociation rate coefficient.

At first order, we can write the perturbation  $\varphi_{ip}$  in the following way:

$$\varphi_{ip} = A_{ip} \frac{1}{T} \frac{\partial T}{\partial \mathbf{r}} \cdot \mathbf{u}_p + B_{ip} \frac{\partial \mathbf{V}}{\partial \mathbf{r}} : \mathbf{u}_p \mathbf{u}_p + D_{ip} \frac{\partial \mathbf{V}}{\partial \mathbf{r}} + G_{ip} + L_{ip} \mathbf{u}_p \cdot \mathbf{d}_p \quad (32)$$

Comparing with the previous expressions for  $\varphi_{ip}$ , we see in Eq.(32) a diffusion term  $L_{ip}$ .

The transport terms of the Navier-Stokes equations may be calculated as above but also the dissociation rate constant at first order; thus we find

$$k_D = \bar{k}_D \left[ 1 - \left( g_{001} + d_{001} \frac{\partial V}{\partial \mathbf{r}} \right) \left( \frac{\bar{E}_V - \bar{E}_{VD}}{kT} \right) \right] \quad (33)$$

Similarly, we find for the vibrational energy at first order

$$E_V = \bar{E}_V \left( 1 + g_{001} + d_{001} \frac{\partial V}{\partial \mathbf{r}} \right) \quad , \quad (34)$$

so that combining (33) and (34), we obtain an expression for the rate constant depending on the vibrational non-equilibrium, i.e.

$$k_D = \bar{k}_D \left[ 1 + \left( \frac{E_V - \bar{E}_V}{\bar{E}_V} \right) \left( \frac{\bar{E}_{VD} - \bar{E}_V}{kT} \right) \right] \quad , \quad (35)$$

where  $\bar{E}_{VD}$  represents the vibrational energy loss due to dissociation (at zero order).

We need a physical model of course in order to have a complete expression: details may be found in Ref.11.

#### 4.2 (SNE)<sub>v</sub>+(SNE)<sub>c</sub> Case

We consider simultaneous vibrational and chemical non-equilibriums. Thus, we have

$$\begin{aligned} J_{TRp}^0 &= 0 \\ \frac{df_{ip}^0}{dt} &= J_{TRp}^1 + J_{vp}^0 + J_{cp}^0 \end{aligned} \quad (36)$$

At zero order, we have simultaneously a vibrational relaxation and a chemical production.

This case has been widely analysed in the past at the macroscopic level [19], [20], [21]: dissociation rate constants are modified and, depending on various assumptions and models, expressions for  $k_D = k_D(T, T_v)$  have been obtained. Similarly, the usual vibrational relaxation equation is modified because of the dissociation.

However, at first order, no important interaction takes place, since the first order terms depend only on rotational relaxation, generally negligible. It is the same for the transport terms which do not depend on vibration (see previous SNE cases). Further discussions may be found in Ref.24.

An example of comparison for the ratio  $V = \frac{k_D(T, T_v)}{\bar{k}_D(T)}$  computed from different models is represented in Fig.5.

#### 4.3 Tentative general solution

In an attempt to unify the calculation methods of relaxing and reacting gas flows at the macroscopic level, we suggest to use the Navier-Stokes equations closed with species conservation equations (kinetic equations) and vibrational relaxation equations taking the chemical reactions into account: this is an SNE formulation, but the reaction rate constants are computed with the WNE model [8].

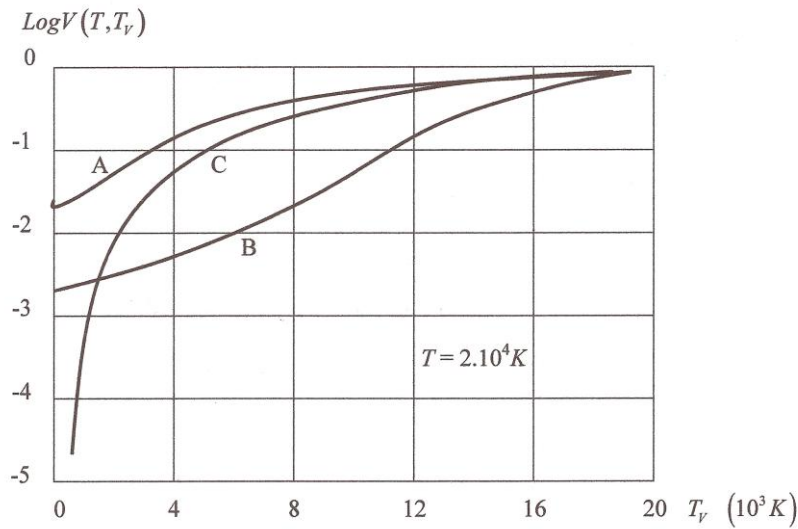
For example, in the simple case of dissociating pure gases, the formula for  $k_D$  is given by Eq.(35) and the relaxation equation may be written as follows, if we use the harmonic oscillator model:

$$\frac{dE_V}{dt} = \frac{E_V - \bar{E}_V}{\tau_v} + (E_V - E_{VD}) k_D n_p \quad (37)$$

The term  $E_{vD}$ , is calculated at first order, like  $k_D$ . We can note that realistic values for  $E_{vD}$  lie in the range  $0.3-0.5 E_D$  [13].

In this framework, the transport terms may be used in their GCE formulation which takes into account the vibrational relaxation. From a general point of view, it is also recommended to use these terms in their dimensionless form, less sensitive to non-equilibrium effects.

Extensions to dissociating-recombining case and to gas mixtures including atomic and molecular components as well as numerous reactions have been carried out. A few examples are given below.



**Figure 5: Vibration-dissociation factor  $V$  for nitrogen,  $T=2.10^4$  K**

A:  $(SNE)_C + (WNE)_V$  Case : Non-preferential anharmonic oscillator model

B:  $(SNE)_C + (WNE)_C$  Case : Preferential model,  $-U = E_D/6k$  [20]

C : Semi-empirical model [21]

## 5.0 APPLICATIONS TO HYPERSONIC FLOWS

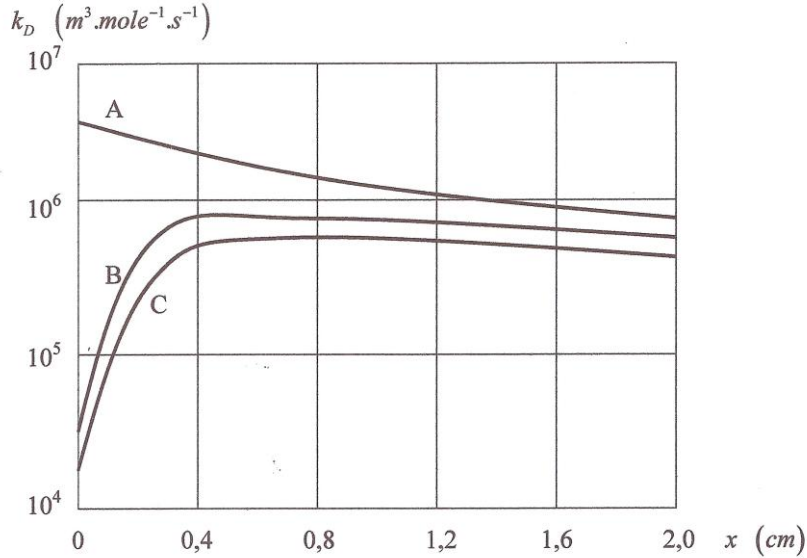
### 5.1 Shock Waves

We consider the flow behind a straight strong shock wave moving in quiescent air, with the following conditions:  $M_s = 25$ ,  $p_0 = 8.5 Pa$ ,  $T_0 = 205 K$ . A classical chemical model including 17 reactions is adopted and the classical Landau-Teller equations for the molecular components are used; however, formulas of the type (35) are used for the chemical rate constants involving dissociation and exchange reactions and the relaxation equations include energy loss (gain) due to chemical reactions (cf Eq.37). One-dimensional Euler equations are also used [12].

An example of variation of a dissociation rate constant ( $N_2$ ) behind the shock is shown in Fig.6 and compared to the corresponding Arrhenius rate constant. Thus, strong differences may be pointed out due to the vibrational relaxation in the region where  $T_v(N_2) < T$ .

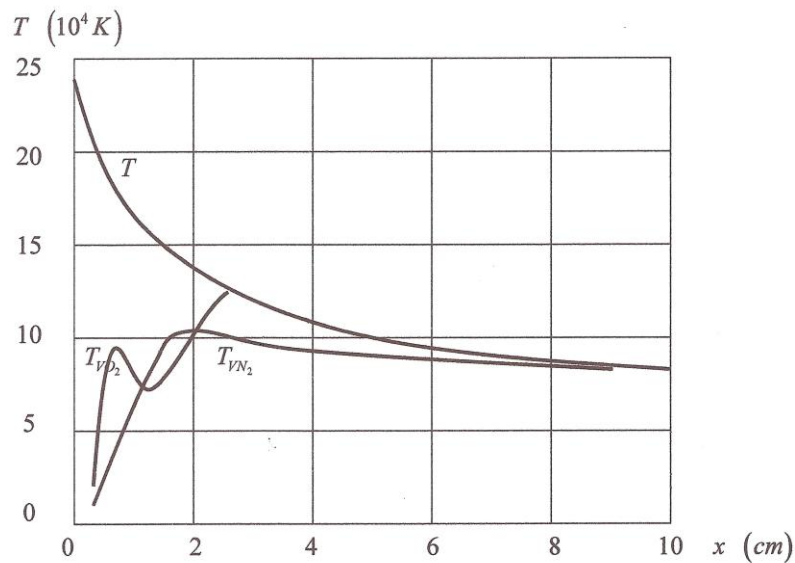
The evolution of the vibrational temperatures is represented in Fig.7 where we can see a minimum for  $T_v(O_2)$  which does not exist without vibration-chemistry interaction.

In order to give an idea about the order of magnitude of the “relaxation pressure”  $p_R$ , the evolution of  $P_R/p$  is represented in Fig.8: thus, close to the shock wave, we see that this ratio is of the order of a few per cent.



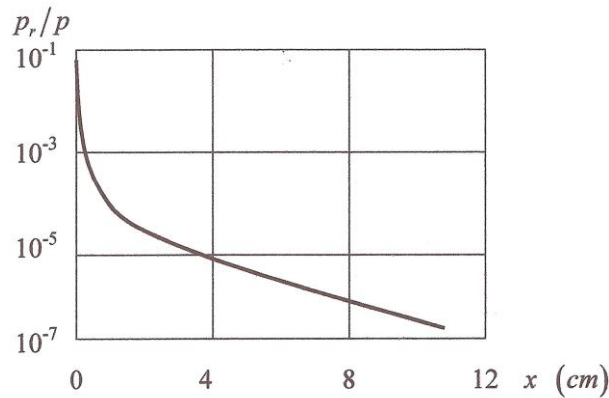
**Figure 6: Dissociation rate constants of nitrogen behind a shock wave in air**  
 $M_s=25$ ,  $p_0=8,5\text{Pa}$ ,  $T_0=205\text{K}$

A:  $k_D$  Arrhenius, B:  $k_D$  with interaction, C:  $k_D$  empirical



**Figure 7: Spatial variation of temperatures behind a shock wave**  
**in air** (Conditions of Fig.6)



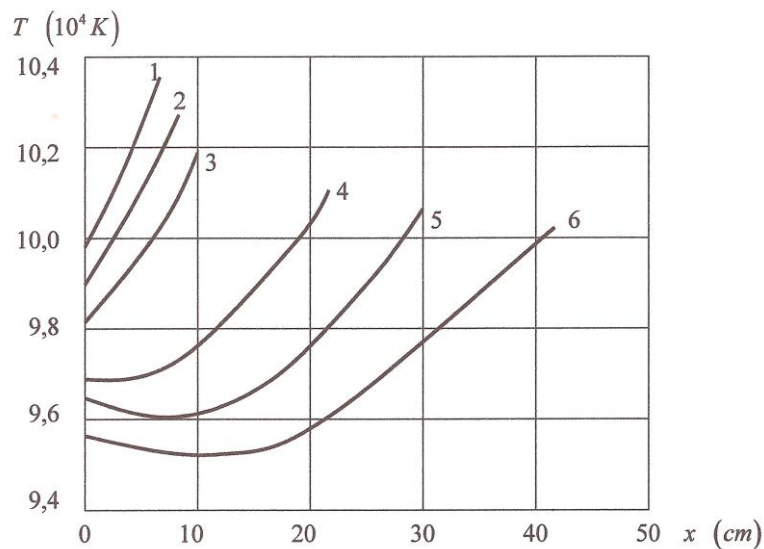


**Figure 8: Relaxation pressure behind a shock wave in air**  
(Conditions of Fig.6)

## 5.2 Boundary Layers

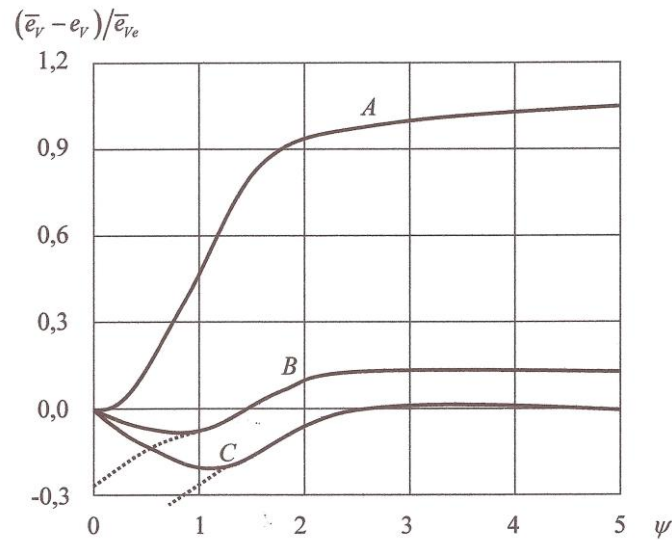
We consider the boundary layer in vibrational and chemical non-equilibrium developing at the end-wall of a shock tube after the reflection of the incident shock wave. The reflected shock wave propagates in the non-equilibrium medium generated by the incident shock wave: an example is represented in Fig.9, [13].

What is of interest here is the behaviour of the rate constants in the end-wall boundary layer; thus, the time evolution of the vibrational non-equilibrium across the boundary layer is represented in Fig.10 in which we can see a vibrational freezing zone ( $T_v > T$ ) appearing some time after the reflection, due to the migration towards the wall of high energy molecules. The result is an increase of the dissociation rate constant in this zone in spite of the decrease of  $T$  (Fig.11). The phenomenon is accentuated when the wall is non-catalytic.



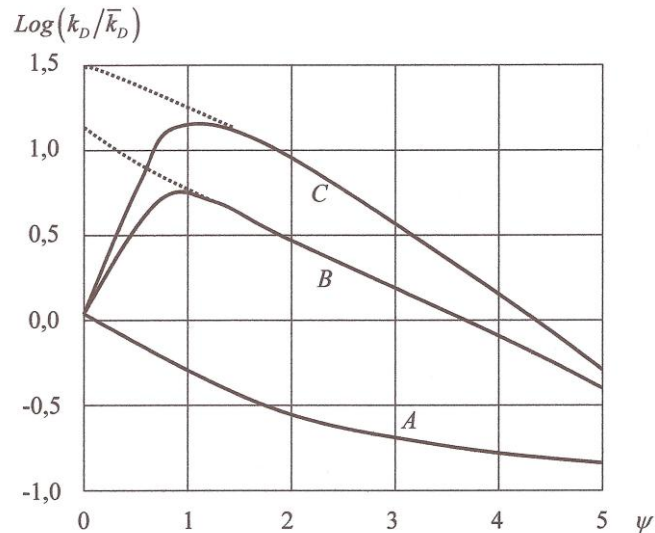
**Figure 9: Temperature distributions behind a reflected shock wave**  
(Nitrogen,  $M_s=12$ ,  $p_0=200\text{Pa}$ )

Time after reflection : 1 :  $15\mu\text{s}$ , 2 :  $25\mu\text{s}$ , 3 :  $40\mu\text{s}$ , 4 :  $400\mu\text{s}$ , 5 :  $500\mu\text{s}$ , 6 :  $600\mu\text{s}$ , 7 :  $700\mu\text{s}$



**Figure 10: Vibrational non-equilibrium distribution across the boundary layer**  
(Conditions of Fig9,  $\psi$  : Von Mises transverse coordinate),  
Time after reflection : A :25 $\mu$ s, B :500 $\mu$ s, C : 900 $\mu$ s

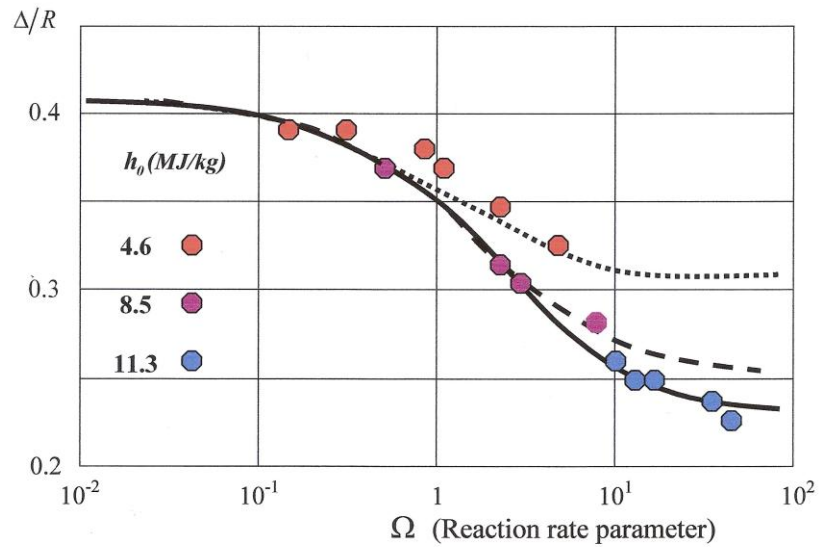
*Full line : Catalytic wall. Dotted line : Non-catalytic wall*



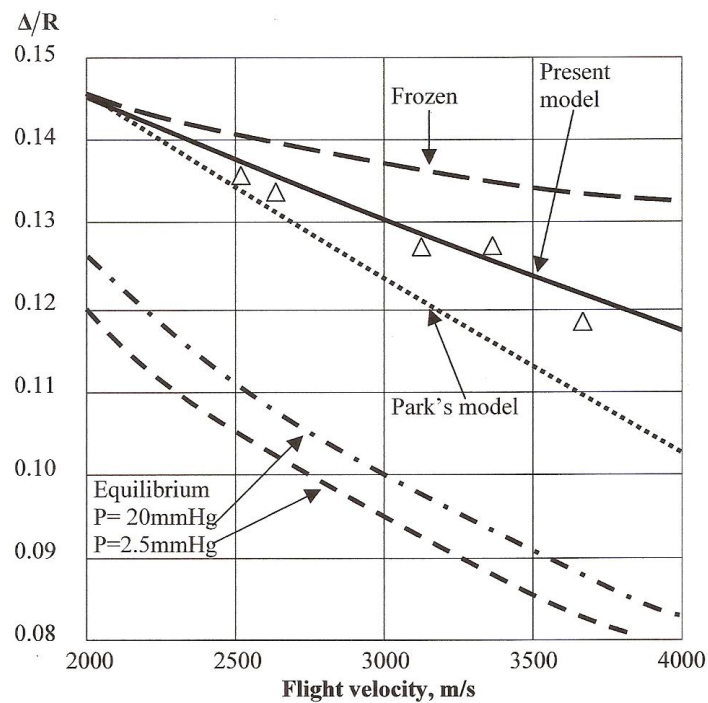
**Figure 11: Dissociation rate constants across the boundary layer**  
(Conditions and notation of Fig.9)

### 5.3 Flows around Bodies

Comparisons of results obtained from Navier-Stokes computations using the present model discussed above with experimental results carried out in shock tunnel and ballistic range are presented in Figs.12 and 13. In fact, they refer to the shock stand-off distance over hemisphere-cylinder bodies: this parameter is sensitive to the non-equilibrium effects, as it may be seen in the figures [14]. The good agreement observed between experimental and simulated values gives support to the reliability of the models used.



**Figure 12: Measured (•) [22] and computed stand-off distances in carbon dioxide flow (shock tunnel)**



**Figure 13: Measured [23] and computed shock stand-off distances**  
 $\rho R = 2.10^{-4} \text{ kg/m}^2$ ,  $\Delta$  : Experiments (gun tunnel)

## 6.0 CONCLUSIONS

Much work remains to be done in the field of kinetic theory of reactive molecular gases: more elaborate models, STS models, inelastic and reactive cross-sections, electronic transitions, direct simulations, complete GCE method, .... The results presented above, however, prove a relative maturation of ideas and methods, so that reliable computations of non-equilibrium flows may be carried out.

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